ABSTRACT

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MOLECULAR ORBITAL CALCULATIONS ON A MINICOMPUTER.

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A program (CINDO, QCPE No. 240) capable of calculating CNDO and INDO wavefunctions for open and closed shell molecules on a medium sized computer (IBM 360/44) was adapted to run on a minicomputer (PDP 11/34 with an RT-11 operating system).

The program was linked into the computer by the overlay method by dividing the program into three overlay regions which allows for a much larger memory space. The program was linked for the closed shell calculations only. By modifying the dimension statement, the matrices were reduced from 50 basis functions to 35. A sample calculation (INDO, CLOSED) was done for formaldehyde to compare the result with that obtained from QCPE. The result shows that the electronic energy was not converging as predicted.

MOLECULAR ORBITAL CALCULATIONS

ON A MINICOMPUTER

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DEDICATION

To my parents Mr. and Mrs. A. O. Fesobi for their guidance, support, understanding and their never ending faith ...

A.B.F.

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INTRODUCTION

The importance of any theory of molecular structure is that it helps build up various physical laws of molecules in agreement with the more basic universal physical laws of motion and interactions. In so doing, the theories attempt a qualitative description of the structure of molecules and their chemical properties based on Schroedinger's equation. However, due to the computational complexities there is need to employ some approximation methods.

The scope of this research thus entails the comprehension of one approximation method's theory and then successfully applying the computational exercise in a minicomputer. This thesis is thus divided into two major sections, the first develops the quantum chemistry approximation and the second discusses the implementation of this calculation on the computer. The implementation aspect involves the conversion of a calculation of CNDO and INDO molecular orbitals written for the IBM system 360/65 digital computer to a minicomputer PDP 11/34 with an RT-11 operating system.

LITERATURE REVIEW

There are two major quantum chemistry approximations. They are Valence Bond theory and Molecular Orbital (MO) theory. This thesis will, however, be exclusively devoted to the MO theory. Amongst those who poineered the work on the MO theory were Hund, Mulliken, Lennard-Jones and Slater.[1] Molecular quantum-mechanical calculations can be divided into two classes: ab initio and semiempirical. Semiempirical calculations generally use a simpler Hamiltonian than the correct molecular Hamiltonian and incorporate into the calculation experimental data or parameters which can be adjusted to fit experimental data. In contrast, an ab initio calculation uses the correct Hamiltonian for the system and attempts a solution without the use of experimental data. An example of the semiempirical method is the Huckel MO treatment of conjugated hydrocarbons, which uses a one-electron Hamiltonian and takes the bond integrals as adjustable parameters rather than quantities to be calculated theoretically, while an example of the ab initio method is a Hartree-Fock Self Consistent Field (SCF) calculation that seeks the antisymmetrized product ϕ of one-electron functions that minimizes $\int\phi^*\hat{H}\phi\partial\tau$, where $\hat{H}$ is the Hamiltonian.

For a one electron molecule, MO theory provides a precise description but only gives a good approximation for a many electron molecule. From classical mechanics, the energy (E) of a system

is the total sum of the kinetic energy, (T) and the potential energy function (V).

Hence,

$$(\hat{T} + \hat{V})\Psi = E\Psi$$

Schroedinger theorized that the correct way to postulate wave character of particles was to replace the kinetic energy and potential energy function with linear operators $\hat{T}$, $\hat{V}$ and to set up a wave equation in the form

$$[T + V]\Psi = E\Psi \qquad (1)$$

The wavefunction Ψ describes the spatial motion of all the particles of the system moving in the field of force indicated by the potential-energy operator $\hat{V}$.[1] For a one electron system like hydrogen moving in the field of a nuclear charge Ze, the potential energy function

$$V = -Ze^2r^{-1} \qquad (2)$$

where r is distance of the electron from the nucleus and e is the unit of electronic charge. Since the coordinate system is centered on the atomic nucleus, one need only consider the kinetic energy of the electron. For a single particle the kinetic energy T is,

$$T = \frac{-h^2}{8\pi^2 m}\nabla^2 \qquad (3)$$

where h is the Planck's constant, m is the electronic mass, and

$$\nabla^2 = \frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2} \qquad (4)$$

in cartesian coordinates.

By substituting equation (2) and (3) into equation (1), the Schroedinger's equation for hydrogen becomes

$$\left[\frac{-h^2}{8\pi^2 m}\nabla^2 - \frac{Ze^2}{r} \right] \Psi(1) = E\Psi(1) \qquad (5)$$

where Ψ is the orbital for only one electron and E is the energy for the system. The linear operator in equation (5) is the Hamiltonian operator, H;

$$\left[\frac{-h^2}{8\pi^2 m}\nabla^2 - \frac{Ze2}{r} \right] \equiv H$$

Schroedinger's equation for a one electron system thus becomes

$$H(1)\Psi(1) = E\Psi(1)$$

For a many electron system where there are N nuclei and n electrons, the many particle Hamiltonian operator H^{Total} is

$$H^{Total}(1,2,\ldots N;\ 1,2,\ldots n) = \frac{-h^2}{8\pi^2} \sum_{1}^{N} M_A^{-1} \nabla_A^2$$

$$+ \sum_{A<B} e^2 Z_A Z_B r_{AB}^{-1} - \frac{h^2}{8\pi m^2} \sum_{1}^{n} \nabla^2_p - \sum\sum_{Ap} e^2 Z_A r_{Ap}^{-1} + \sum_{p<q} e^2 r_{pq}^{-1}$$

where M_A is the mass of nucleus A, m and e are electronic mass and charge respectively, $Z_A e$ is the charge on nucleus A, and r_{ij} is the distance between particles i and j. By summing indices A and B over atomic nuclei and those including p and q over electrons, the Schroedinger equation for the whole system becomes

$$H^{Total}(1,2...,N;\ 1,2,...,n)\Psi\ (1,2,...,N;\ 1,2,...,n) = E\Psi(1,2...,N;\ 1,2..., n).^2$$

The full Schroedinger equation will possess an infinite number of solutions but only certain of them will be acceptable physically. For Ψ to be physically reasonable it must be continuous, single valued, and vanish at infinity. The acceptable solutions of the Schroedinger equation must have certain energies labelled E_1, E_2, ... etc. corresponding to wavefunctions Ψ_1, Ψ_2, ... etc. Hence,

$$H^{Total}\psi_i = E_i\Psi_i \qquad (6)$$

where E_i are called the eigenvalues and Ψ_i are the eigenfunctions. If two or more wavefunctions correspond to identical energies, then such solutions are termed degenerate.[1]

In solving Schroedinger's equation, it is usual to divide the wavefunction into two parts, one part representing the electrons and the other representing the nuclei. This is reasonable due to

the fact that the nuclear masses are several thousand times larger than the masses of the electrons, so that the nuclei move very slowly and are essentially static relative to the electrons. This simplified analysis is referred to as the Born-Oppenheimer approximation. The Born-Oppenheimer approximation[1] thus amounts to separating the nuclear kinetic energy and nuclear-nuclear repulsion from H^{Total} and taking into consideration only the part of the Hamiltonian which depends on the position but not the moments of the nuclei. Therefore the Hamiltonian (electronic) operator (H^{el}) becomes

$$H^{el} = \frac{-h^2}{8\pi m^2 p} \Sigma \nabla_p^2 - \Sigma\Sigma e^2 Z_A r_{AP}^{-1} + \sum_{p<q} e^2 r_{pq}^{-1} \qquad (7)$$

The total energy is then

$$H = E + \sum_{A<B} e^2 Z_A Z_B r_{AB}^{-1}$$

where E is the electronic energy and the summation term is the internuclear repulsion energy.

For a normalized wavefunction,

$$\int \Psi_i^2(1)\, d\tau_1 = 1 \qquad (8)$$

where $d\tau$ is the volume element for the electron. For a many particle wavefunction

$$\int \ldots \int \Psi_i^2(1,2, \ldots) d\tau_1\, d\tau_2 \ldots = 1 \qquad (9)$$

where the $d\tau_i$ are the volume elements for each particle in the system. The functions Ψ_i and Ψ_j are mutually orthogonal, i.e.

$$\int \Psi_i \Psi_j \, d\tau = 0. \tag{10}$$

By combining equations (9) and (10) one has

$$\int \Psi_i \Psi_j \, d\tau = \delta_{ij} \tag{11}$$

where δ_{ij} is the Kronecker delta.

Another property is that the quantum mechanical expectation value of any observable, e.g. B, can be denoted by

$$\int \Psi_i^* \, B\Psi_i \, d\tau.$$

Thus for the energy, the expectation value of the Hamiltonian operator can be expressed as

$$E_i = \int \Psi_i^* \, H\Psi_i \, d\tau \tag{12}$$

just as the dipole moment of a system is the expectation value of the dipole moment operator.

Using the Dirac notation, the above can be expressed as

$$\langle \Psi_i | M | \Psi_j \rangle = \int \Psi_i^* M \Psi_j \, d\tau$$

If the operator M has the property

$$\langle \Psi_i | \hat{M} | \Psi_j \rangle = \langle \Psi_j | \hat{M} | \Psi_i \rangle,$$

then the operator $\hat{M}$ is said to be Hermitian.

Two operators $\hat{A}$ and $\hat{B}$ are said to commute if $\hat{A}\hat{B} = \hat{B}\hat{A}$. It follows that if two operators commute, then there are a set of functions which are simultaneoulsy eigenfunctions of both operators, i.e., $A\Lambda_i = l_i\Lambda_i$ and $B\Lambda_i = m_i\Lambda_i$, where l_i and m_i are the eigenvalues.

For the MO theory, the concern is on the operators that commute with the Hamiltonian, H and the eigenfuctions of H are the wavefunctions Ψ_i. Another property is that the off-diagonal matrix elements of the operators M are zero, i.e.

$$\langle\Psi_i|\hat{H}|\Psi_j\rangle = 0,$$

when $\hat{M}$ commutes with the Hamiltonian. Examples of operators that commute with the Hamiltonian are the angular momentum operators $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$, and certain other symmetry operators.

One of the methods of solving Schroedinger's equation is the variation method.[2] The governing principle behind the variation method is that for a Hamiltonian operator $\hat{H}$, where Ψ is any normalized well behaved function that satisfies the boundary conditions, then

$$\int\Psi^*\hat{H}\Psi\, d\tau \geq E_0 \qquad (13)$$

where E_0 is the lowest true eigenvalue of $\hat{H}$.

For n electron system the total wavefunctions is $\Psi(1,2, \ldots, n) = \Psi(1)\Psi(2) \ldots \Psi n(n)$ where the Ψ_i are the orbitals of individual electrons and the product is called the Hartee product. Whereas an orbital gives a complete specification of the spatial

distribution of an electron, it fails to give a specific state of each electron spin. If the spin angular momentum is represented by S, where S_x, S_y and S_z are the components, the spin angular momentum operators all compute with the Hamiltonian operator $\hat{H}$. S_x, S_y and S_z all commute with the spin squared operator $\hat{S}^2$ but do not commute with each other. The spin angular momentum is quantized where each component can take either of the values $\pm \frac{h}{4\pi}$. These two spin states are represented by two mutually orthogonal spin wavefunctions $\alpha(\xi)$ and $\beta(\xi)$ being the spin coordinate. The quantization condition is

$$S^2\eta(\xi) = S(S+1)\eta(\xi)$$

$$S_z\eta(\xi) = m_s\eta(\xi)$$

where $\eta(\xi)$ can be $\alpha(\xi)$ or $\beta(\xi)$ and m_s can have the value $\pm\frac{1}{2}$ in units of $\frac{h}{2\pi}$. M_s assumes the values S, S-1, ..., -S. For a many electron system, the total spin operators S^2 and S_z are given by,

$$S^2 = S_x^2 + S_y^2 + S_z^2$$

$$S_z = \sum_p S_{pz}$$

where the summation runs over all electrons in the system and the corresponding eigenvalues the eigenfunction of S^2 and S_z becomes

$$S^2\Psi = S(S+1)\Psi \qquad (14)$$

and

$$S_z\Psi = M_s\Psi \qquad (15)$$

for only the positive values in equation (14).

The multiplicity of a state is defined as the number of M_S components possible. For $S = \frac{1}{2}$ (doublet state) $M_S = +\frac{1}{2}$ and $-\frac{1}{2}$, and for $S = 1$ (triplet state) $M_S = 1, 0, -1$.

Introducing a mathematical framework for detailed calculation of molecular orbitals, a set of atomic functions

ϕ_μ, $\mu = 1,2 \ldots$, for different atoms that make up the molecules are incorporated in the equation.[3]

$$\Psi_i = C_{1i}\,\Phi 1 + C_{2i}\,\Phi 2 + C_{3i}\,\Phi 3 + \ldots$$

where the $C_{\mu i}$ are numerical coefficients that can have a sign that is real or complex. The above expansion is called the Linear Combination of Atomic Orbitals (LCAO). The solution to the Schroedinger's equation may be rewritten in the form

$\Phi(r, \theta, \Phi) = R_{nl}(r)\, Y_{lm}(\theta, \Phi)$ where r, θ, Φ are the spherical polar coordinates.

$Y_{lm}(\theta, \Phi)$ are known as the spherical harmonics.

$$Y_{lm}(\theta, \Phi) = \theta_{lm}(\theta)\Phi_m(\Phi)$$

$$\theta_{lm}(\theta) = \left[\frac{(2l + 1)(l-m)!}{2(l+m)!}\right]^{\frac{1}{2}} P_{lm}(\cos\theta)$$

$$\Phi_m(\Phi) = \begin{cases} (2\pi)^{-\frac{1}{2}} & m=0 \\ (\pi)^{-\frac{1}{2}} \cos m\phi & m\neq 0 \end{cases}$$

$$\Phi_{\bar{m}}(\phi) = (\pi)^{-\frac{1}{2}} \sin m\phi$$

where $P_{\ell m}(\cos\phi)$ are associated Lengendre polynomials. The

quantum number ℓ (orbital angular momentum) is known as the azimuthal quantum number which has the values 0, 1, 2 ... The quantum number m (magnetic quantum number) takes the $(2\ell + 1)$ values ℓ, $\ell - 1$ ... $-(\ell - 1)$, $-\ell$. The atomic orbitals are labelled by letters according to the value of ℓ; s, p, d and f are assigned $\ell = 0, 1, 2, 3$.

A type of atomic orbital used in the LCAO method is the Slater orbitals and they are used in the calculation. The Slater orbitals are constructed by not altering the 1s function ϕ_{1s} but replacing the 2s function ϕ_{2s} by the linear combination.

$$\phi'_{2s} = (1-S^2_{1s,2s})^{-1/2} (\phi_{2s} - S_{1s,2s}\phi_{1s})^4$$

where $S_{1s,2s}$ is the overlap integral $\int\phi_{1s}(1)\phi_{2s}(1)d\tau$, ϕ'_{2s} is normalized and orthogonal to ϕ_{1s}.

Self-Consistent Field Molecular Orbital Theory--By considering MO theory from ab initio point of view, this section involves the actual calculation of orbitals for the many electron system based on the variational principle. For a closed shell configuration, the expectation value of the energy can be expressed by $\langle\Psi|\hat{H}|\Psi\rangle$.

For a two electron system, the Hamiltonian can be split into two parts

$$H = H_1 + H_2$$

where

$$H_1 = \sum_p H^{core}(p)$$

with $H^{core}_{(p)} = -\frac{1}{2}\nabla_p^2 - \sum_A Z_A r_{pA}^{-1}$

and $H_2 = \sum_{p<q} \sum r_{pq}^{-1}$

where H^{core} is the one electron Hamiltonian representing a motion of an electron in the field of bare nuclei.

Since H^{core} is spin independent, integration over the spin coordinates of electron 1 gives a factor of one and the result is

$$\langle \Psi | H_1 | \Psi \rangle = 2 \sum_{i=1}^{n} H_{ii}$$

where H_{ii} is the expectation value of the molecular orbital Ψ_i,

$$H_{ii} = \int \Psi_i(1)^* H^{core} \Psi_i(1) \, d\tau_1.$$

If electrons 1 and 2 are assigned to different spatial molecular orbitals Ψ_i and Ψ_j with a spin α or β, then there will be four contributions to the repulsion term with each equal to $\frac{1}{2}J_{ij}$ where

$$J_{ij} = \int\int \Psi_i^*(1) \; \Psi_j^*(2) \; \frac{1}{r_{12}} \; \Psi_i(1) \; \Psi_j(2) \; d\tau_1 \, d\tau_2$$

The first and fourth contributions both give $-\frac{1}{2}K_{ij}$ where

$$K_{ij} = \int\int \Psi_i^*(1) \; \Psi_j^*(2) \; \frac{1}{r_{12}} \; \Psi_j(1) \; \Psi_i(2) \; d\tau_1 \; d\tau_2$$

the negative sign is due to the parity difference. By adding up the terms, the electronic energy becomes

$$E = 2\sum_i^n H_{ii} + \sum_i J_{ii} + \sum_{ij(\neq i)}^{n} \sum^{n} (2J_{ij} - K_{ij}) \qquad (16)$$

Since $K_{ii} = J_{ii}$ equation (16) becomes

$$E = 2\sum_{i}^{n} H_{ii} + \sum_{ij}^{nn} (2J_{ij} - K_{ij})$$

where J_{ij} and K_{ij} are known as the coulomb integrals and exchange integrals respectively, H_{ii} is the energy of an electron in a molecular orbital Ψ_i in a field of bare nuclei. Since there are two electrons in an orbital, it is multiplied by 2.

According to the variational principle, the best molecular orbitals are achieved by varying the contribution of the individual one-electron functions $\Psi_1, \Psi_2, \Psi_3, \ldots \Psi_n$ in the determinant of the coefficient until the minimum value of energy is achieved.[2] Such orbitals are called the self consistent, or Hartree-Fock molecular orbitals. The eigenvalues of the Hartree-Fock Hamiltonian operator are expressed as

$$E_i = H_{ii}^{core} + \sum_{j}^{n} (2J_{ij} - K_{ij})$$

which are known as the orbital energies. For the MO for open shell systems[4] where there are q β electrons and p(>q) α electrons, the the wavefunction is expressed as

$$^{p-q+1}\Psi = |\Psi_1(1)\alpha(1)\Psi_1(2)\beta(2) \ldots \Psi_q(2q)\beta(2q)\Psi_{q+1}(2q+1)\alpha(2q+1) \ldots \Psi_{(p+q)}\alpha_{(p+q)}|$$

where p-q+1 is the multiplicity. Wavefunctions of this type are

termed restricted single determinants. Since the total number of α electrons differ from the total number of β electrons, to assign the same spatial orbital to each spin involves a distorted description of the spatial distribution. Hence, a more representative way is to assign two completely independent sets of molecular orbitals, ψ^{α}_1, ψ^{α}_2, ..., ψ^{α}_p and ψ^{β}_1, ψ^{β}_2, ..., ψ^{β}_q, and the wavefunction becomes

$$p\text{-}q + 1\psi = |\psi^{\alpha}_1(1)\alpha(1)\ \psi^{\beta}_1(2)\beta(2)\psi^{\alpha}_2(3)\alpha(3)$$

$$\ldots\ \psi^{\beta}_q(2q)\beta(2q)\psi^{\alpha}_{q+1}(2q+1)\alpha(2q+1)\psi^{\alpha}_{q+2}(2q+2)\alpha(2q+2)$$

$$\ldots\ \psi^{\alpha}_{p+q}(p+q)\ (p+q)\ |$$

This is termed the unrestricted single determinant.[5] In the unrestricted molecular orbital the expectation value of the one electron part is

$$\langle\psi|H_1|\psi\rangle = \sum_{i=i}^{p+q} H_{ii} \quad \text{and the electronic energy is}$$

$$E = \sum_{i=i}^{p+q} H_{ii} + \tfrac{1}{2}\left(\sum_{i}^{p+q}\sum_{j}^{p+q} J_{ij} - \sum_{ij}^{pp} K^{\alpha}_{ij} - \sum_{ij}^{qq} K_{ij}{}^{\beta}\right)$$

If the one electron energies for an α orbital is

$$E^{\alpha}_i = H^{\alpha}_{ii} + \sum_{j}^{p}(J_{ij} - K^{\alpha}_{ij}) + \sum_{j}^{q} J_{ij},$$

then the total energy is given by

$$E = \tfrac{1}{2}\sum_{i}^{p}(E^{\alpha}_{i} + H^{\alpha}_{ii}) + \tfrac{1}{2}\sum_{i}^{q}(E^{\beta}_{i} + H^{\beta}_{ii}). \qquad (17)$$

Semiempirical--Approximate molecular orbital theories are semiempirical, in that molecular properties are made to agree with experimental data. The CNDO (complete neglect of differential overlap) semiempirical was developed by Pople, Santry and Segal.[6] In this method only the bonding or valence electrons are treated explicitly, whereas the nonbonding or inner shell electrons are treated as part of a rigid core. Thus they modify the nuclear potential in the one-electron part of the Hamiltonian. The basic approximations of the CNDO method are:

Approximation 1: Replacting the overlap matrix by the unit matrix in the Roothaan equations and neglecting the overlap integrals $S_{\mu\upsilon}$ in normalizing the molecular orbitals.

Approximation 2: Neglecting differential overlap in all two electron integrals so that

$$(\mu\upsilon/\lambda\sigma) = \delta_{\mu\upsilon}\delta_{\lambda\sigma}\ (\mu\mu/\lambda\lambda)$$

Approximation 3: Reducing the remaining set of coulomb-type integrals to one value per atom pair,

$$(\mu\mu/\lambda\lambda) = \gamma_{AB} \qquad \phi_{\mu} \text{ on A}, \phi_{\lambda} \text{ on B}$$

Approximation 4: Neglecting monoatomic differential overlap (in an invariant manner) in the interaction integrals involving the cores of other atoms

$$(\mu/V_{\beta}/\upsilon) = \delta_{\mu\upsilon}\ V_{AB}$$

Approximation 5: Taking diatomic off

diagonal core matrix elements to be proportional to the corresponding overlap integrals

$H_{\mu\upsilon} = \beta_{\alpha\beta}{}^{o} \; S_{\mu\upsilon} \quad \phi_\mu$ on A, ϕ_υ on B[1]

The definition for the above symbols are: $(\mu\upsilon/\lambda\sigma) = \delta_{\mu\upsilon}\delta\lambda\sigma \; (\mu\mu/\lambda\lambda)$ is the zero differential overlap approximated where $(\mu\upsilon/\lambda\sigma) = \int\int\phi_\mu(1)\phi_\upsilon(1)\frac{1}{r_{12}}\phi_\lambda(2)\phi\sigma(2)d_{\tau 1}d_{\tau 2}$; γ_{AB} is the average electrostatic repulsion between any electron on atom A and any electron on atom B where $\gamma_{AB} = \int\int S_A^2(1)(r_{12})^{-1}S_B^2(2)d\tau_1 d\tau_2$ and V_{AB} is interaction of any valence electron on atom A with the core of atom B where $V_{AB} = Z_B\int S_A^2(1)(r_{1B})^{-1}d\tau_1$. The effect of this CNDO approximation is that it allows the energy to be broken down into monatomic and diatomic contributions,

$$E_{total} = \Sigma E_A + \sum_{A<B} E_{AB},$$

where $E_A + \sum_{\mu}^{A} P_{\mu\mu}U_{\mu\mu} + \frac{1}{2}\sum_{\mu}^{A}\sum_{\upsilon}^{A}(P_{\mu\mu}P_{\upsilon\upsilon} - \frac{1}{2}P_{\mu\mu}{}^2)$

and $E_{AB} = \sum_{\mu}^{A}\sum_{\upsilon}^{B}(2P_{\mu\upsilon}\beta_{\mu\upsilon} - \frac{1}{2}P_{\mu\upsilon}{}^2\gamma_{AB}) +$

$$(Z_A Z_B R_{AB}{}^{-1} - P_{AA}V_{AB} - P_{BB}V_{BA} + P_{AA}\gamma_{AB})$$

For large intermolecular separations, the potential integral V_{AB}, V_{BA} and γ_{AB} all approximate to $R_{AB}{}^{-1}$. Hence the last group of the term becomes $Q_A Q_B R_{AB}{}^{-1}$ where Q_A and Q_B are the net charge on atom A and B respectively and R_{AB} is the distance between atoms A and B. The CNDO/I and CNDO/II parameterization are the two methods

used in obtaining the overlap integrals $S_{\mu\upsilon}$, the core Hamiltonian element $U_{\mu\mu}$, V_{AB} the electron repulsion integrals γ_{AB}, and the bonding parameters β_{AB}.[6] The CNDO/II method differs from CNDO/I in the way it treats the penetration integrals and the one center atomic core integrals. The penetration integrals are expressed as $(Z_B\gamma_{AB} - V_{AB})$ where Z_B is the nuclear charge on atom B.

INDO (Intermediate Neglect of Differential Overlap)--This method makes provision for different interactions that actually take place between two electrons with parallel or opposite spins.[7] In CNDO the spin interaction is neglected but it has an effect, especially if both electrons are on the same atom. If two electrons in different atomic orbitals on the same atom have parallel spins they exhibit a small repulsion energy.

$$(\mu\upsilon/\mu\upsilon) = \int\int \phi_\mu(1)\phi_\mu(2)\frac{1}{r_{12}}\phi_\upsilon(1)\phi_\upsilon(2)d\tau_1 d\tau_2$$

$\mu \neq \upsilon$ where ϕ_μ and ϕ_υ are on the same atom. In CNDO this integral is neglected and all interactions between two electrons on atom A are replaced by γ_{AA} (for $\gamma_{AA} = \int\int S_A^2(1)(r_{12})^{-1}S_A^2(2)d\tau_1 d\tau_2$) no matter what their spin is. INDO makes provision for this repulsion energy.

NDDO (Neglect of Diatomic Differential Overlap)--This method mainly involves the retention of the dipole-dipole interactions. Calculations at this level have been performed by Sustmann et al.[8]

EXPERIMENTAL

Implementing Program on Minicomputer--A Fortran-IV computer program for CNDO and INDO calculations was obtained from Indiana University chemistry department (Quantum Chemistry Program Exchange (QCPE) Program No. 240).[9] This program is named CINDOM. CINDOM is a CNDO and INDO Molecular Orbital Program for medium sized computers. CINDOM is a modification of QCPE 141 which has the capability of computing CNDO wavefunctions for open and closed shell molecules containing the elements hydrogen to chlorine and INDO open and closed shell calculations for molecules containing the elements hydrogen to flourine.

The matrices are large enough to allow calculations for molecules containing up to 20 atoms and 50 basis functions. By modifying the dimension statements, calculations for molecules with up to 70 basis functions can be performed on computers with a storage capacity less than that required by QCPE 141 for identical size problems.

In brief, the description, instruction and properties of CINDOM, as obtained from QCPE, are outlined as follows.

Description of Program and Input Data for CINDOM--The matrices in the program are large enough to allow molecules containing up to 20 atoms or 50 basis function. One atomic orbital basis function is allowed for hydrogen (1s), four each for elements lithium

through flourine (2s, $2p_x$, $2p_y$, and $2p_z$), and nine each for the elements sodium through chlorine (3s, $3p_x$, $3p_y$, $3p_z$, $3d_{z^2}$, $3d_{xy}$, $3d_{yz}$, $3d_{x^2-y^2}$).

Operation of the Program--In MAIN, input data for calculation is read in the following formats: First Line: Identification and comments; Second Line: The methods, columns 1-4 should contain either "CNDO" or "INDO" and columns 6-9 should contain either "OPEN" or "CLSD" depending on the type of calculation desired. Third Line: NATOMS (Number of atoms), CHARGE and MULTIP (Multiplicity), FORMAT (3I4); Next NATOMS Line: AN (Atomic Number), X, Y, Z, (cartesian coordinates) of each atom, one atom to a line, Format (I4, 3(3X,F12.7)). These lines are followed by a blank line if another set of data for another calculation is desired. If otherwise, a line with -01 in columns 1-3 specifying end of the data follows.

After reading the molecular data the main program calls the subroutines COEFFT and INTGRL which compute the integrals used in the molecular orbital calculation. It then calls the subroutines which perform the MO calculation (HUCKCL, SCFCLO, CPRINT for closed-shell molecules, HUCKOP, SCFOPN, OPRINT for open shell molecule). The qualitative description of the operation of each subroutine is thus:

COEFFT assigns the coefficients used in the calculation of overlap and coulomb integrals. The vectors, Y(9135) and Z(765) of QCPE 141, containing these coefficients have been replaced by vectors containing only the non-zero coefficients Y(224) and

Z(87). Two vectors IY(224) and IZ(87) have been added which identify the indices of the non-zero coefficients. In subroutine INTGRL the overlap matrix (stored in the first array of (COMMON/ ARRAYS/) and the coulomb integral (υ_{AB}) matrix (stored in COMMON/ GAB/) are computed. The subroutines SS, HARMTR, RELVEC, FACT, BINTGS, AINTGS and MATOUT are called by subroutine INTGRL. The method of integral evaluation is described in reference 1. Integrals are calculated for pairs of atoms using a local diatomic coordinate system. The rotation matrix formed in subroutine HARMTR is then used to transform the overlap integrals to the molecular coordinate system. Subroutine HUCKCL first forms a ZDO extended Huckel type approximation to the Fock matrix with diagonalized elements formed from $-\frac{1}{2}(I+A)$ where I and A are the ionization potential and electron affinity respectively, and off-diagonal elements formed from $(\beta^{\circ}_{A}\ \beta^{\circ}_{B})S_{\mu\upsilon}/2$ where β°_{A} is the bonding parameter that depends only on atom A. This matrix is diagonalized and an initial density matrix is constructed. At this point the corrections to the Hamiltonian are added for CNDO and INDO calculations if one of these options is desired. Since EIGN only works on the lower half of the matrix to be diagonalized, the core Hamiltonian in the closed shell segments is stored in the upper half of matrix A with the diagonal terms stored in a seperate 50 elements linear array.

Subroutine SCFCLO takes as input the initial density matrix and the CNDO or INDO core Hamiltonian. The Fock matrix is formed by first adding the CNDO integrals and then INDO corrections to

these integrals depending upon which option is used. The Fock matrix is diagonalized and a new density matrix is formed which is used to construct a new Fock matrix. This procedure is repeated until the electronic energy converges to 10^{-6}. At this point, the Fock matrix is printed, then diagonalized once more and the resulting eigenvectors are printed. The electronic energy is computed after each new Fock matrix is formed and before it is diagonalized. A limit of 25 iterations is allowed (IT = 25).

Subroutine CPRINT computes dipole moments, atom densities and nuclear repulsion energy. HUCKOP is similar to HUCKEL except that alpha and beta density matrices are formed from the initial Huckel eigenvectors. The core Hamiltonian is stored in its entirety in the third matrix of COMMON/ARRAYS/. The symmetrical alpha and beta density matrices are stored by putting p^{α} in the lower left triangle including the diagonal elements of the second matrix in COMMON/ARRAYS/ while p^{β} is stored in the upper triangle with its diagonal terms stored PDIAG.[10] Subroutine SCFOPN has the same structure as SCFCLO except that it has to handle p^{α}, p^{β}, F^{α}, and F^{β}. All are stored as described above for the p matrices. The Fock matrices are formed simultaneously and then each half is separately diagonalized.

Subroutine OPRINT calculates the same properties as CPRINT. In addition, this segment forms a spin density matrix and from this computes isotropic hyperfine coupling constants (for H, C, N, O, and F). The proportionality constant relating spin density to

coupling constants are for INDO calculations only. The subroutines SS, HARMTR, RELVEC, FACT, BINGTS, AINTGS and MATOUT are called only by INTGRL. Subroutines EIGN, SCFOUT and EIGOUT are needed in the subroutines HUCKEL through OPRINT. The above has been the description of QCPE program No. 240. The purpose of this project is to convert the QCPE program to a minisize computer.

The Atlanta University chemistry department has a digital computer PDP 11/34 with an RT-11 operating system. Because of the memory size required for this calculation, certain modifications had to be made in the program in order for the system to be able to perform the CINDOM calculation. The memory size of this minicomputer is approximately 50 kbytes of program memory space. In using the system, the Single Job monitor (SJ) is used. It is preferable to the time sharing monitor because it has the fastest response time (at interrupt and keyboard level) and the minimum memory requirements of all the standard RT-11 monitors.

In developing a program, the procedure illustrated in Fig. 1 must be utilized. The text editor (EDIT) is used to locate text to be changed, and to execute and verify the changes. It can also list an edited page on the console terminal and output a page of text to the output file. To compile, the FORTRAN command (/FORTRAN) invokes the FORTRAN language processor to compile the associated files. The The OBJ file helps show which lines have errors.

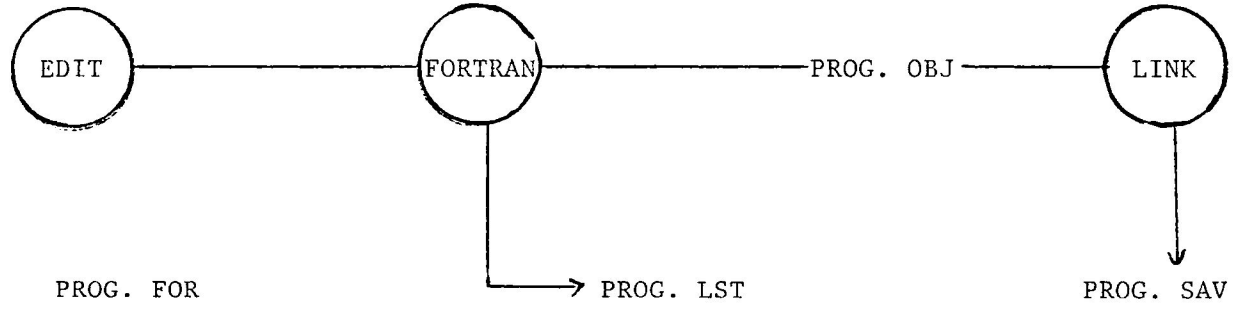

Fig. 1. Fortran File.

The linker processes the object modules of the main program and subroutines to:

> Relocate each object module and assign absolute addresses.
>
> Link the modules by correlating global symbols that are defined in one module and references in another. Create an overlay structure if specified and include the necessary run-time overlay handlers and tables. Also searches libraries specified to locate unresolved globals. It also produces a symbol defintion file.[11]

The program CINDOM is now named CNINDO. The MAIN is renamed CNDO for convenience. The first stage is editing to reduce the program size in any way possible without affecting the results or its accuracy, but reducing the memory space. Program CINDOM is in double precision. In standard Fortran a "storage unit" is the about of space that represents a real figure. A storage unit corresponds to 1 word. One (1) word is equivalent to 16 bits which corresponds to 2 bytes. A figure in double precision occupies 4 words and has 15 digits, however, a single precision figure occupies 2 words and has 7 digits. Thus the conversion of double precision values to single precision value helps save valuable memory space. Hence, to reduce the memory space all double precision values are changed to single precision. By changing values from double precision to single precision the accuracy of the values is not affected. However, it reduces the number of digits from fifteen to seven. Examples of some of the changes made are

IMPLICIT REAL * 8(A-H, O-Z) ⟶ IMPLICIT REAL * 4(A-H, O-Z)

64.DO ⟶ 64.00
DMAXO ⟶ MAXO
DFLOAT ⟶ FLOAT
DSQRT ⟶ SQRT
etc. ⟶ etc.

During editing certain commands were changed to fit the language of the system, e.g.

WRITE ⟶ TYPE
READ ⟶ ACCEPT
etc. ⟶ etc.

In the subroutine COEFFT there was a need to create a data file in order to save storage space. The object of this procedure was to insure that during the running of the program the data file could be called but would not be involved in consuming memory space in the actual program. The non-zero coefficients U(224), Z(87), and the vectors IY(224), IZ(87) were created as four new data files named YCNDO.DAT, ZCNDO.DAT, IYCNDO.DAT, IZCNDO.DAT, respectively. In subroutine COEFF a CALL ASSIGN was made for each data file and indicated during the execution of the program. The next step was the compilation stage where the program was denoted by the command FORTRAN FILE.FOR/LIST. This created the OBJ File. The purpose of the .LST file is to be able to detect what line and what kind of error there is. After debugging all the non-logical errors, the subroutines are compiled using the command FORTRAN/NOLINENUMBERS/ OPTIMIZE:CSE FILE.FOR. This command is used to help reduce the memory space needed. The command /NOLINENUMBERS helps suppress

generation of internal sequence numbers. The command /OPTIMIZE: selects optimization level with value supplied used to enable certain optimizations when desired, and CSE to enable common subexpression elimination. An example of what this command does is that the computer will be able to do a particular operation that occurs frequently just once and then when such operations are needed, it is simply executed. The size of the MAIN (CNDO) necessitates the use of the command /UNITS:n; which allows a maximum of n simultaneously open I/O channels at run time. In this case, n has the value 12 since n can be (1<n<15).

The next stage is LINK. The ability of the system to use an overlays linkage provides much larger memory space. The overlay method is used to link the subroutines since direct link will cause the program to exceed the memory space available. The overlay linkage method allows portions of the program (called overlay segments) to reside on a storage disk.[11] The overlay scheme is a multi-region arrangement that allows one to store any number of subroutines or functions in a region and then call such functions or subroutines as they are needed. The overlay system is constructed for the CNINDO program with a root segment that is always memory-resident. CNDO and BLOCK are the current memory-resident overlay segment and other subroutines in the overlay segments are stored in the backup storage device. The root segment contains the transfer address, stack space, impure variables, data and variables needed by other different segments; it must therefore not be overlaid. The "calling"

scheme by the program used in the design of the overlay segments is illustrated in Fig. 2.

There is a distinct area for each overlay region. The overlay segments are brought into memory as they are needed. Segments that overlay each other must be logically independent. If a subroutine calls another subroutine then they must reside in different overlay region (in other words the components of another segment with which it shares address space)or else the original segment will be lost. Overlay segments that share both the same physical memory location and address space form a region as diagramed in Fig. 3, for the example CNINDO. The overlay regions to the linker is specified with the /O option. Linkage is thus:

```
        R   LINK

*     CNINDO, DK:  CNINDO  =  CNDO, BLOCK/I/C
*     COEFFT/0:1/C
*     INRFEL/0:1/C
*     HUCKCL/0:1/C
*     SCFCLO/0:1/C
*     CPRINT/0:1/C
*     SS/0:2/C
*     RELVEC/0:2/C
*     HARMTR/0:2/C
*     EIGN/0:2/C
*     SCFOUT/0:2/C
*     FACT/0:2/C
*     MATOUT/0:2/C
*     AINTGS/0:3/C
*     BINTGS/o:3/C
*     EIGOUT/0:3
LIBRARY SEARCH  ?  $SHORT
```

To conserve memory space, the subroutines for the OPEN SHELL calculations were not linked. Also in linking, the number of basis functions that the program is capable of handling was reduced from

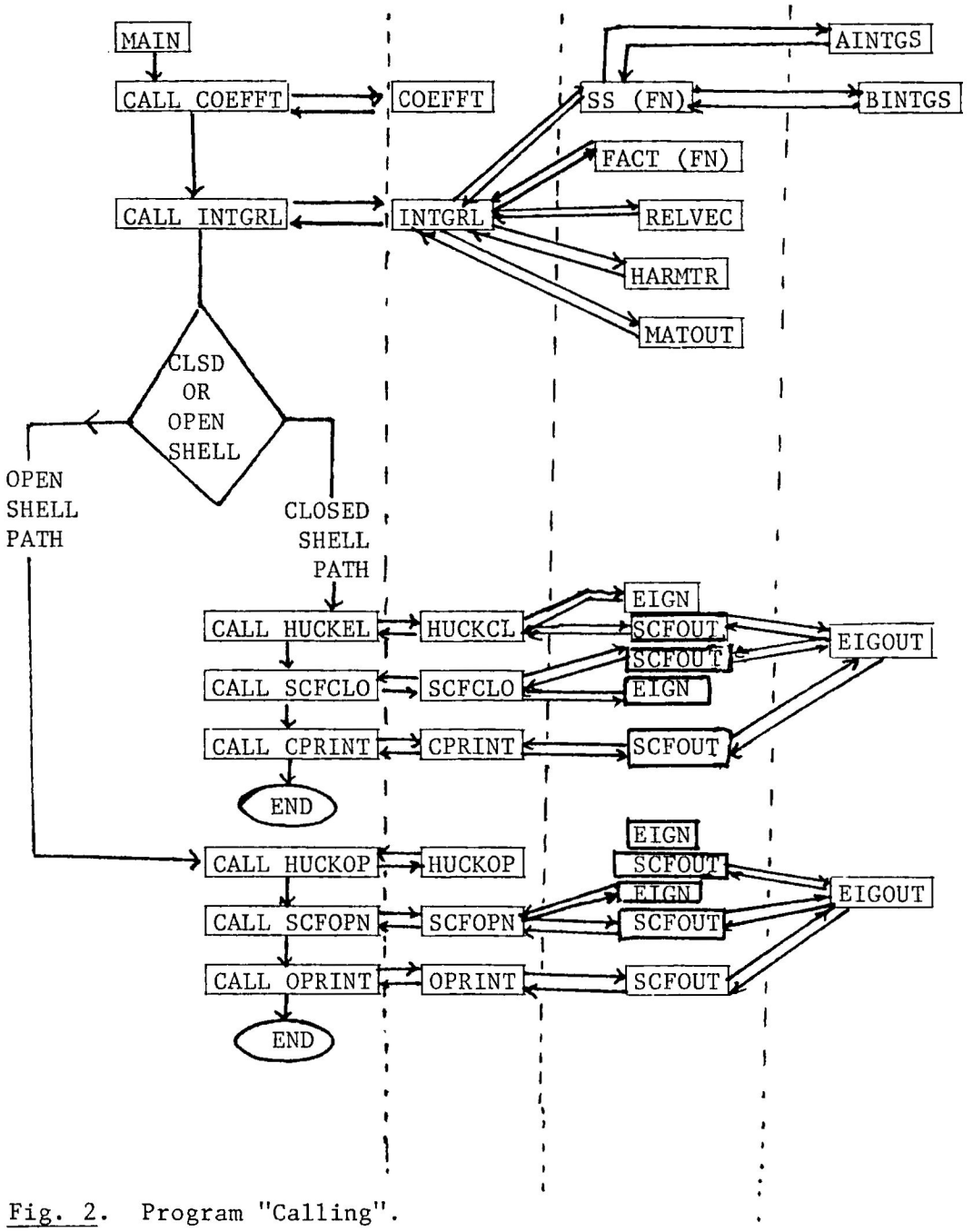

Fig. 2. Program "Calling".

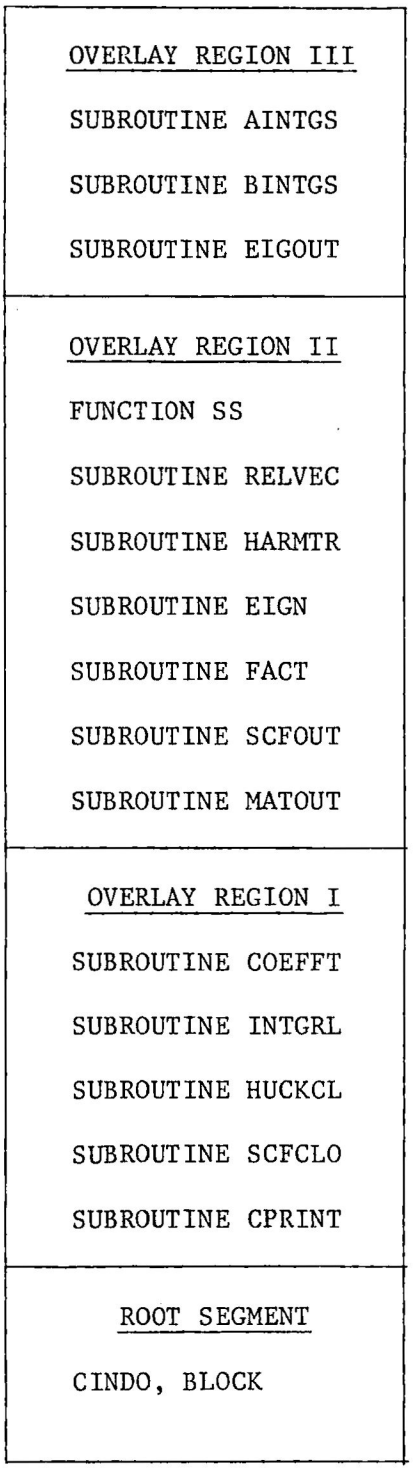

Fig.3. Overlay Linkage.

50 to 35. This was accomplished by modifying the dimension statements.

RESULTS

The result of a sample calculation for formaldehyde is shown in Fig. 4. The calculation used the INDO approximation and formaldehyde, in the ground state, has a closed shell configuration. For this calculation the carbon atom was placed at the origin, the oxygen atom along the z axis, and the hydrogen atoms were in the x - z plane. These results were compound with the test results sent with the program CINDOM. The overlap integral

$$S_{\mu\nu} = \int \Phi_{\mu}(1)\Phi_{\nu}(2)d\tau_1$$

For example, in this calculation the overlap integral between the 2s orbitals of carbon and oxygen equalled 0.3743. The coulomb integral matrix elements are given by

$$\gamma_{AB} = \int\int S_A^2(1)(\gamma_{12})^{-1}S_B^2(2)d\tau_1 d\tau_2$$

In this calculation, for example, the coulombic integral between the carbon and the oxygen equalled 0.5903.

In this calculation the core Hamiltonian, given by

$$H_{\mu\nu} = \int \phi_{\mu}(1)H^{core}\phi_{\mu\nu}(1)d\tau$$

equalled -0.35675 for the carbon 2s and oxygen 2s orbitals. All of the above values agreed exactly with the test results sent with the program CINDOM. However, in our calculation the electronic

energy did not converge. Therefore, the succeeding results were incorrect.

The Hartree-Fock energy matrix elements are given by

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - 1/2P_{\mu\mu})\gamma_{AA} + \sum_{B\neq A}(P_{BB\ AB} - V_{AB})$$

$$F_{\mu\nu} = B_{AA}S_{\mu\nu} - Y_2 P_{\mu\nu}\gamma_{AB}$$

For example, in this calculation the H-F energy element between the 2s of the carbon and the 2sx of the oxygen was equal to 0.00636. A typical density matrix element ($P_{\mu\nu} = \sum_{i}^{acc} C_{\mu i} C_{\mu i}$) was 1.74270 corresponding to the electron density of the carbon 2s orbital. The eigenvectors and eigenvalues correspond to the molecular orbitals and their respective energies. They are expressed as linear combinations of the atomic orbitals i.e., $X_i = \sum_{\mu} C_{\mu i}\phi_{\mu}$. For example the lowest energy molecular orbital has an energy of -1.48746 A. U. and had a coefficient of -0.57434 from the carbon 2s orbital, -0.66577 from the oxygen 2s orbital, etc. The total binding energy was equal to 0.02717 A. U. and shows the molecule to be stable. The dipole moment shows the major component to be along the z axis, in the direction of the carbon-oxygen bond as is expected.

CONCLUSION

A sample calculation for formaldehyde is presented in Fig. 4. The test problem was for INDO CLOSED, to test the result with that obtained from CINDOM. The OVERLAP INTEGRAL, COULOMB INTEGRAL and CORE HAMILTONIAN were the same for both CINDOM and CNINDO. The electronic energy and other calculations were different. From the result obtained for CNINDO the electronic energy is not converging. The reason that we are not obtaining the correct answer might be due to some errors still not found in the program. However, the most probable source of error is that our calculation was performed using single precision arithmetic (> digit precision) and the CINDOM calculation was performed in double precision arithmetic (15 digit precision).

```
 ./RUN CNINDO
 INPUT IS READ IN THE FOLLOWING ORDER
 (1) AN IDENTIFICATION LINE WHICH IS PRINTED IN THE OUTPUT
 (2) OPTION(WAVE FUNCTION OPTION) AND OPNCLO(OPEN OR CLOSED SHELL)
     THE FORMAT IS A4,1X,A4 AND THE KEY WORDS ARE)
     FOR THE WAVE FUNCTION(A4)  CNDO  INDO
     FOR THE OPEN-CLOSED OPTION(A6)  OPEN  CLSD
 (3) NATOM,CHARGE,MULTIP  FORMAT(3I4)
 (4) ATOMIC NUMBER,X COORD.,Y COORD.,Z COORD.-
     1 LINE ENTRY/ATOM FORMAT(I4,3(3X,F12.7))
 (5) IF ANOTHER PROBLEM FOLLOWS,THIS LINE ENTRY IS BLANK.
     IF END OF DATA ENTER -01 IN COLUMNS 1-3.
 FORM
      IM
 INDO CLSD
      DO.  SD
    1   0   1

   4 ATOMS   CHARGE =   0   MULTIPLICITY =   1

    6
   6       0.0000000       0.0000000       0.0000000
    8                                       1.22
   8        0.0000000       0.0000000       1.2200000
    1          .73531                        -.54
   1        0.9353100       0.0000000       -0.5400000
    1         -.73531                        -.54
   1       -0.9353100       0.0000000       -0.5400000
 YCNDO.DAT
 ZCNDO.DAT
 XYCNDO.DAT
 XZCNDO.DAT
```

	1	2	3	4	5	6	7	8	9	10
1	1.0000	0.0000	0.0000	0.0000	0.3734	0.0000	0.0000	-0.3079	0.5245	0.5245
2	0.0000	1.0000	0.0000	0.0000	0.0000	0.2146	0.0000	0.0000	0.4257	-0.4257
3	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.2146	0.5000	0.0000	0.0000
4	0.0000	0.0000	0.0000	1.0000	0.4580	0.0000	0.0000	-0.3056	-0.2458	-0.2458
5	0.3734	0.0000	0.0000	0.4580	1.0000	0.0000	0.0000	0.0000	0.0840	0.0840
6	0.0000	0.2146	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0401	-0.0401
7	0.0000	0.0000	0.2146	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
8	-0.3079	0.0000	0.0000	-0.3056	0.0000	0.0000	0.0000	1.0000	-0.0754	-0.0754
9	0.5245	0.4257	0.0000	-0.2458	0.0840	0.0401	0.0000	-0.0754	1.0000	0.1616
10	0.5245	-0.4257	0.0000	-0.2458	0.0840	-0.0401	0.0000	-0.0754	0.1616	1.0000

COULOMB INTEGRAL MATRIX

	1	2	3	4
1	0.5903	0.4101	0.4368	0.4368
2	0.4101	0.8265	0.2649	0.2649
3	0.4368	0.2649	0.2590	0.2810
4	0.4368	0.2649	0.2810	0.7500

CORE HAMILTONIAN

		1	2	3	4	5	6	7	8	9	10
1	1	-5.80912	0.00000	0.00000	0.00000	-0.35675	0.00000	0.00000	0.29336	-0.28914	-0.28914
2	1	0.00000	-5.49497	0.00000	0.00000	0.00000	-0.20507	0.00000	0.00000	-0.23467	0.23467
3	1	0.00000	0.00000	-5.49497	0.00000	0.00000	0.00000	-0.20507	0.00000	0.00000	0.00000
4	1	0.00000	0.00000	0.00000	-5.49497	-0.43766	0.00000	0.00000	0.29204	0.13549	0.13549
5	2	-0.35675	0.00000	0.00000	-0.43766	-7.32321	0.00000	0.00000	0.00000	-0.06176	-0.06176
6	2	0.00000	-0.20507	0.00000	0.00000	0.00000	-6.83126	0.00000	0.00000	-0.02945	0.02945
7	2	0.00000	0.00000	-0.20507	0.00000	0.00000	0.00000	-6.83126	0.00000	0.00000	0.00000
8	2	0.29336	0.00000	0.00000	0.29204	0.00000	0.00000	0.00000	-6.83126	0.05541	0.05541
9	3	-0.28914	-0.23467	0.00000	0.13549	-0.06176	-0.02945	0.00000	0.05541	-4.25659	-0.05346
10	4	-0.28914	0.23467	0.00000	0.13549	-0.06176	0.02945	0.00000	0.05541	-0.05346	-4.25659

ELECTRONIC ENERGY -40.7265090942

ELECTRONIC ENERGY -40.2547454834

ELECTRONIC ENERGY -40.3137855530

ELECTRONIC ENERGY -40.5690885315

ELECTRONIC ENERGY -40.2698135376

ELECTRONIC ENERGY -38.7307054443

ELECTRONIC ENERGY -40.1576805115

ELECTRONIC ENERGY -40.2747840881

ELECTRONIC ENERGY -40.3720831409

ELECTRONIC ENERGY -41.2467384338

ELECTRONIC ENERGY -40.9423614502

ELECTRONIC ENERGY -40.6429672241

ELECTRONIC ENERGY -41.1105842590

ELECTRONIC ENERGY -41.1796302795

ELECTRONIC ENERGY -42.7173070544

ELECTRONIC ENERGY -40.2743911743

ELECTRONIC ENERGY -43.1275444031

ELECTRONIC ENERGY -41.2204780579

ELECTRONIC ENERGY -42.1497077942

ELECTRONIC ENERGY -40.6655349731

ELECTRONIC ENERGY -39.7317352295

ELECTRONIC ENERGY -41.0326004028

ELECTRONIC ENERGY -41.2558326721

ELECTRONIC ENERGY -41.8885421753

ELECTRONIC ENERGY -39.9657020569

ELECTRONIC ENERGY -41.3758087158

HARTREE-FOCK ENERGY MATRIX

		1	2	3	4	5	6	7	8	9	10
1	1	-0.57979	-0.00443	0.00001	-0.00944	-0.40773	0.00636	0.00008	0.44923	-0.32564	-0.33444
2	1	-0.00443	-0.62074	0.00001	0.00652	-0.00052	-0.20530	-0.00000	0.00225	-0.22318	0.24667
3	1	0.00001	0.00001	-0.12739	-0.00001	-0.00000	-0.00000	-0.28362	0.00001	0.00001	0.00002
4	1	-0.00944	0.00652	-0.00001	-0.14341	-0.54026	-0.00319	-0.00005	0.28199	0.13316	0.14193
5	2	-0.40773	-0.00052	-0.00000	-0.54026	-0.87962	-0.00020	-0.00000	-0.02368	-0.05834	-0.05889
6	2	0.00636	-0.20530	-0.00000	-0.00319	-0.00020	-0.20942	0.00000	0.00431	-0.03077	0.02796
7	2	0.00008	-0.00000	-0.28362	-0.00005	-0.00000	0.00000	-0.28165	0.00013	0.00004	0.00003
8	2	0.44923	0.00225	0.00001	0.28199	-0.02368	0.00431	0.00013	-0.07812	0.10199	0.10059
9	3	-0.32564	-0.22318	0.00001	0.13316	-0.05834	-0.03077	0.00004	0.10199	-0.47769	0.07471
10	4	-0.33444	0.24667	0.00002	0.14193	-0.05889	0.02796	0.00003	0.10059	0.07471	-0.48235

EIGENVALUES AND EIGENVECTORS

		EIGENVALUES	-1.48746	-0.77122	-0.69797	-0.48599	-0.35044	-0.27926	-0.14436	0.09299	0.09674	0.48859
			1	2	3	4	5	6	7	8	9	10
1	1		-0.55424	0.03012	-0.43983	-0.00006	-0.56903	0.14961	0.00492	0.03737	-0.00487	-0.38722
2	1		0.00011	-0.73650	-0.00057	0.00002	0.04707	-0.01286	-0.00045	0.57770	-0.33477	-0.00491
3	1		0.00001	-0.00009	0.00007	-0.62035	-0.00691	-0.00041	-0.78129	-0.00002	-0.00001	0.00005
4	1		-0.38491	-0.04771	0.42658	-0.00014	0.44041	0.42481	-0.00399	-0.03202	-0.00162	-0.59926
5	2		-0.66577	-0.35631	0.51097	0.00023	-0.05691	-0.40070	0.00059	0.00699	0.00359	0.35859
6	2		0.00195	-0.20928	-0.00273	0.00001	-0.34151	-0.01652	0.00038	-0.70830	-0.65445	-0.00262
7	2		0.00001	-0.00001	0.00012	-0.78432	0.00535	-0.00028	0.62033	0.00004	-0.00004	-0.00013
8	2		0.25750	-0.01239	0.20868	0.00042	-0.21264	-0.68285	0.00188	0.01595	0.01284	-0.61555
9	3		-0.19578	-0.38839	-0.43801	0.00002	0.44214	-0.20838	-0.00380	-0.31271	0.40972	-0.05188
10	4		-0.20259	0.48160	-0.34879	0.00007	0.48397	-0.29451	-0.00420	0.24848	-0.46860	-0.05539

DENSITY MATRIX

		1	2	3	4	5	6	7	8	9	10
1	1	1.74189	-0.05009	0.00775	-0.42572	0.25570	0.04468	-0.00620	-0.44086	-0.00988	-0.06267
2	1	-0.05009	1.10369	-0.00069	0.03015	-0.00218	0.38299	0.00048	-0.01593	0.68994	-0.60239
3	1	0.00775	-0.00069	0.75977	-0.00620	0.00089	0.00057	0.97304	0.00301	-0.00595	-0.00659
4	1	-0.42572	0.03015	-0.00620	1.27969	0.43024	-0.05062	0.00480	-0.73667	-0.00065	-0.05202
5	2	0.25570	-0.00218	0.00089	0.43024	1.74270	0.01649	-0.00064	0.44114	0.03807	0.03962
6	2	0.04468	0.38299	0.00057	-0.05062	0.01649	0.13999	-0.00046	0.03618	0.19775	-0.26154
7	2	-0.00620	0.00048	0.97304	0.00480	-0.00064	-0.00046	1.22038	-0.00249	0.00476	0.00514
8	2	-0.44086	-0.01593	0.00301	-0.73667	0.44114	0.03618	-0.00249	1.24135	-0.06646	-0.06406
9	3	-0.00988	0.68994	-0.00595	-0.00065	0.03807	0.19775	0.00476	-0.06646	1.31936	0.60859
10	4	-0.06267	-0.60239	-0.00659	-0.05202	0.03962	-0.26154	0.00514	-0.06406	0.60859	1.43117

TOTAL ENERGY = -23.5773259209

BINDING ENERGY = 0.7221739721 A.U.

1	4.3[illegible]045
2	4.[illegible]1423
3	1.[illegible]7369
4	1.[illegible]1171

DIPOLE MOMENTS

COMPONENTS	X	Y	Z
ELECTRONIC	0.592290	0.000000	11.589194
[illegible]	0.[illegible]291	-0.032917	0.499454
[illegible]	0.[illegible]000	0.000000	0.000000
[illegible]	0.[illegible]291	-0.032917	12.088648

DIPOLE MOMENT= 12.[illegible] DEBYES

Fig. 4. Results of an INDO Calculation on Formaldehyde.

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